Porosity Engineering of Boron Nitride Materials for Hydrogen Storage

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論　文　の　要　旨

Our society is running on fossil fuels for over two centuries. With the tremendous consumption of these carbon-rich fossil fuels, the fixed carbon underground is releasing to our atmosphere; the concentration of CO_2 in our atmosphere is continually rising. This produces long-term effects and threatens our environment, makes it unpredictable, and possibly disastrous. Thus, searching for “green” fuels that can substitute fossil fuels is on the urgent agenda. Among the candidates for future clean fuels and energy, H_2 attracts particular attentions due to its zero-pollutant emission during the consumption. However, realization of the practical applications of hydrogen still presumes a lot of challenges facing by the scientific community. Hydrogen must be firstly produced, subsequently stored and then delivered to an end user. In this chain, the bottle-neck problem is how to store H_2 efficiently and safely. Traditional storage methods relied on compressed gas cylinders, which are themselves require an energy-consuming process and have notable safety risks. To date, most of H_2 storage is based on physisorption, chemisorption and chemical reactions. Physisorption is featured by the quick adsorbing and releasing kinetics, excellent reversibility, and cycling ability. Many researchers focused on the novel designs and found new H_2 adsorbents relying on the physisorption mechanism and employing its advantages. And my project related to a design of advanced porous boron nitride (BN) nanomaterials for H_2 storage, from this viewpoint, is meaningful and important.

Compared to traditional porous carbons and metal-organic frameworks (MOFs), porous BNs exhibit unique thermostability and resistance to chemicals, which can improve their cycling and regeneration performances during H_2 storage. However, the state of development of reliable methods to prepare porous

BN materials is not that optimistic at present; there were no reports on porous BNs with a specific surface area (SSA) >1000 m^2 g^{-1} before 2012 (the starting time of my PhD project). This situation also makes BNs far less known within the scientific community with respect to their H_2 storage potentials. In my dissertation, I focus on the development of easily operable, one-step, and template-free reactions to fabricate porous BN nanomaterials, and using these porous BNs for H_2 detailed storage studies. The fundamental material textural factors responsible for their H_2 sorption behaivors are also carefully explored and discussed.

I will firstly introduce hierarchically porous BN microbelts with the SSA ranging from 1144 to 1488 m^2 g^{-1}, which were the first BN materials in the world with the SSA exceeding 1000 m^2 g^{-1}. They were synthesized by a one-step reaction of boric acid-melamine (2B·M) adducts in ammonia at temperatures varied from 900 to 1100 ^oC. Comprehensive characterizations including high-resolution transmission electron microscopy, X-ray diffraction, and Raman confirmed the obtained BN phase is partially disordered, shows an enlarged average (0002) spacing of 0.38 nm, larger than the normal 0.33 nm for a bulk *h*-BN. By changing the synthesis conditions, the textures of the prepared porous BNs are adjustable. It was demonstrated that these high-surface-area BN porous belts exhibit high and reversible hydrogen uptakes from 1.6 to 2.3 wt %.

Next, the synthesis of a series of microporous BN microsponges *via* this simple one-step template-free reaction will be introduced. The products showed increased interlayer (0002) distances compared to the standard *h*-BN and revealed special dislocation structures. The SSAs and pore volumes of these BN microsponges could be effectively tuned in a wide range (920−1900 m^2 g^{-1} and 0.516−1.070 cm^3 g^{-1}, respectively) by changing the synthetic conditions. Amazingly, there were almost no macro- and mesopores in these obtained BN microsponge products. Decent and totally reversible H_2 uptakes, from 1.65 to 2.57 wt % at 1 MPa and 77 K, were confirmed for these BN materials. Finally, I carried out the systematical studies of the correlations between the textural parameters of these novel materials and their H_2 sorption capacities.

Besides, I also made a modification of the synthetic conditions for BN microbelts to prepare composition-changed microbelts, namely porous BCNO microbelts. Three BCNO microbelt sample series were featured by similar morphologies, chemical compositions as well as partially disordered phases. Furthermore, they also showed high and close SSAs, pore volumes, but distinct ultra-narrow pore widths that varied from 0.4 to 1.1 nm. Enhanced H_2 uptakes of 1.90–2.14 wt % at 1 MPa and 1.41–1.60 wt % at a lower pressure of 0.1 MPa were recorded for these materials. And importantly, I revealed the correlation between pore width and H_2 storage performances of the present BCNO porous materials.

Over all, I have developed a simple strategy for the fabrication of highly porous BNs, and prepared a series of new porous BN materials with different porosity (hierarchically porous and microporous) and chemical (BN and BCNO) features. They exhibited very high SSAs and pore volumes, and H_2 uptake capacities up to 2.6 wt % at 1 MPa and 77 K, which corresponded to a gravimetric energy capacity of ~0.87 kWh kg^{-1}. I hope my work will inspire many researchers in this field to design and search for better porous BN H_2 accumulators.

審　　査　　の　　要　　旨

〔批評〕

Several important issues have been risen by the Committee members. These included the questions on how the chemistry environment is important for hydrogen adsorption; what is the difference between adsorption in carbon and BN materials; what is the difference between the chemical and physical adsorption; what determines the reversibility of the hydrogen release; how actually H_2 molecules are bound with BN surfaces; how to control the pore width experimentally; what is the difference of the prepared structures from conventional turbostratic materials; what is the ratio of sp^3 to sp^2 bonds in the fabricated porous materials; what determines the width of X-ray peaks on the XRD patterns taken from porous BN. Also the outlook of the applicant on the possible increase in surface area from the achieved 1900 m^2/g to the required 5000-7000 m^2/g was particularly examined.

〔最終試験結果〕

平成 27 年 2 月 18 日、数理物質科学研究科学位論文審査委員会において審査委員の全員出席のもと、著者に論文についての説明を求め、関連事項につき質疑応答を行った。その結果、審査委員全員によって、合格と判定された。

〔結論〕

上記の論文審査ならびに最終試験の結果に基づき、著者は博士（工学）の学位を受けるに十分な資格を有するものと認める。